EXAMPLE 1.2 Identifying orbitals from quantum numbers

Which set of orbitals is defined by $n = 4$ and $l = 1$? How many orbitals are there in this set?

Answer We need to remember that the principal quantum number n identifies the shell and that the orbital quantum number l identifies the subshell. The subshell with $l = 1$ consists of p orbitals. The allowed values of $m_l = l, l - 1, \ldots, -l$ give the number of orbitals of that type. In this case, $m_l = +1$, 0, and -1. There are therefore three 4p orbitals.

Self-test 1.2 Which set of orbitals is defined by the quantum numbers $n = 3$ and $l = 2$? How many orbitals are there in this set?

(c) Electron spin

Key points: The intrinsic spin angular momentum of an electron is defined by the two quantum numbers s and m_s. Four quantum numbers are needed to define the state of an electron in a hydrogenic atom.

In addition to the three quantum numbers required to specify the spatial distribution of an electron in a hydrogenic atom, two more quantum numbers are needed to define the state of an electron. These additional quantum numbers relate to the intrinsic angular momentum of an electron, its **spin**. This evocative name suggests that an electron can be regarded as having an angular momentum arising from a spinning motion, rather like the daily rotation of a planet as it travels in its annual orbit around the sun. However, spin is a quantum mechanical property and this analogy must be viewed with great caution.

Spin is described by two quantum numbers, s and m_s. The former is the analogue of l for orbital motion but it is restricted to the single, unchangeable value $s = \frac{1}{2}$. The magnitude of the spin angular momentum is given by the expression $\{s(s + 1)\}^{1/2}\hbar$, so for an electron this magnitude is fixed at $\frac{1}{2}\sqrt{3}\hbar$ for any electron. The second quantum number, the **spin magnetic quantum number**, m_s, may take only two values, $+\frac{1}{2}$ (anticlockwise spin, imagined from above) and $-\frac{1}{2}$ (clockwise spin). The two states are often represented by the two arrows ↑ ('spin-up', $m_s = +\frac{1}{2}$) and ↓ ('spin-down', $m_s = -\frac{1}{2}$) or by the Greek letters α and β, respectively.

Because the spin state of an electron must be specified if the state of the atom is to be specified fully, it is common to say that the state of an electron in a hydrogenic atom is characterized by four quantum numbers, namely n, l, m_l, and m_s (the fifth quantum number, s, is fixed at $\frac{1}{2}$).

(d) Nodes

Key point: Regions where wavefunctions pass through zero are called nodes.

Inorganic chemists generally find it adequate to use visual representations of atomic orbitals rather than mathematical expressions. However, we need to be aware of the mathematical expressions that underlie these representations.

Because the potential energy of an electron in the field of a nucleus is spherically symmetric (it is proportional to Z/r and independent of orientation relative to the nucleus), the orbitals are best expressed in terms of the spherical polar coordinates defined in Fig. 1.8. In these coordinates, the orbitals all have the form

$$\psi_{nlm_l} = \overbrace{R_{nl}(r)}^{\text{Variation with radius}} \times \overbrace{Y_{lm_l}(\theta,\phi)}^{\text{Variation with angle}} \qquad (1.5)$$

This expression expresses the simple idea that a hydrogenic orbital can be written as the product of a function $R(r)$ of the radius and a function $Y(\theta,\phi)$ of the angular coordinates. The positions where either component of the wavefunction passes through zero are called **nodes.** Consequently, there are two types of nodes. **Radial nodes** occur where the radial component of the wavefunction passes through zero and **angular nodes** occur where the angular component of the wavefunction passes through zero. The numbers of both types of node increase with increasing energy and are related to the quantum numbers n and l.

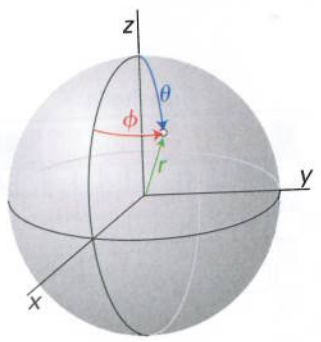

Figure 1.8 Spherical polar coordinates: r is the radius, θ (theta) the colatitude, and ϕ (phi) the azimuth.

(e) The radial variation of atomic orbitals

Key point: An s orbital has nonzero amplitude at the nucleus; all other orbitals (those with $l > 0$) vanish at the nucleus.

Figures 1.9 and 1.10 show the radial variation of some atomic orbitals. A 1s orbital, the wavefunction with $n = 1$, $l = 0$, and $m_l = 0$, decays exponentially with distance from the nucleus and never passes through zero. All orbitals decay exponentially at sufficiently great distances from the nucleus and this distance increases as n increases. Some orbitals oscillate through zero close to the nucleus and thus have one or more radial nodes before beginning their final exponential decay. As the principal quantum number of an electron increases, it is found further away from the nucleus and its energy increases.

An orbital with quantum numbers n and l in general has $n - l - 1$ radial nodes. This oscillation is evident in the 2s orbital, the orbital with $n = 2$, $l = 0$, and $m_l = 0$, which passes through zero once and hence has one radial node. A 3s orbital passes through zero twice and so has two radial nodes. A 2p orbital (one of the three orbitals with $n = 2$ and $l = 1$) has no radial nodes because its radial wavefunction does not pass through zero anywhere. However, a 2p orbital, like *all* orbitals other than s orbitals, is zero at the nucleus. For any series of the same type of orbital, the first occurrence has no radial nodes, the second has one radial node, and so on.

Although an electron in an s orbital may be found at the nucleus, an electron in any other type of orbital will not be found there. We shall soon see that this apparently minor detail, which is a consequence of the absence of orbital angular momentum when $l = 0$, is one of the key concepts for understanding chemistry.

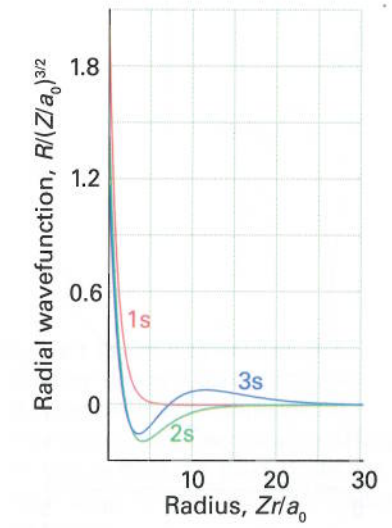

Figure 1.9 The radial wavefunctions of the 1s, 2s, and 3s hydrogenic orbitals. Note that the number of radial nodes is 0, 1, and 2, respectively. Each orbital has a nonzero amplitude at the nucleus (at $r = 0$).

EXAMPLE 1.3 Predicting numbers of radial nodes

How many radial nodes do 3p, 3d, and 4f orbitals have?

Answer We need to make use of the fact that the number of radial nodes is given by the expression $n - l - 1$ and use it to find the values of n and l. The 3p orbitals have $n = 3$ and $l = 1$ and the number of radial nodes will be $n - l - 1 = 1$. The 3d orbitals have $n = 3$ and $l = 2$. Therefore, the number of radial nodes will $n - l - 1 = 0$. The 4f orbitals have $n = 4$ and $l = 3$ and the number of radial nodes will be $n - l - 1 = 0$. The 3d and 4f orbitals are the first occurrence of the d and f orbitals so this also indicates that they will have no radial nodes.

Self-test 1.3 How many radial nodes does a 5s orbital have?

(f) The radial distribution function

Key point: A radial distribution function gives the probability that an electron will be found at a given distance from the nucleus, regardless of the direction.

The Coulombic (electrostatic) force that binds the electron is centred on the nucleus, so it is often of interest to know the probability of finding an electron at a given distance from the nucleus, regardless of its direction. This information enables us to judge how tightly the electron is bound. The total probability of finding the electron in a spherical shell of radius r and thickness dr is the integral of $\psi^2 d\tau$ over all angles. This result is written $P(r)\,dr$, where $P(r)$ is called the **radial distribution function.** In general,

$$P(r) = r^2 R(r)^2 \qquad (1.6)$$

(For s orbitals, this expression is the same as $P = 4\pi r^2\psi^2$.) If we know the value of P at some radius r, then we can state the probability of finding the electron somewhere in a shell of thickness dr at that radius simply by multiplying P by dr. In general, a radial distribution function for an orbital in a shell of principal quantum number n has $n - 1$ peaks, the outermost peak being the highest.

Because the wavefunction of a 1s orbital decreases exponentially with distance from the nucleus and the factor r^2 in eqn 1.6 increases, the radial distribution function of a 1s orbital goes through a maximum (Fig. 1.11). Therefore, there is a distance at which the electron is most likely to be found. In general, this most probable distance decreases as the

Figure 1.10 The radial wavefunctions of the 2p and 3p hydrogenic orbitals. Note that the number of radial nodes is 0 and 1, respectively. Each orbital has zero amplitude at the nucleus (at $r = 0$).